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Lime - Natural Pozzolan Conservation Mortars: Parameters that Affect Reactivity and Strength

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Abstract The natural pozzolans studied are commercial products and come from the volcanic islands of Milos and Kimolos as well as North Greece mainland. The materials were characterised mineralogically and chemically by XRD and SEM/EDX respectively, while their reactivity with calcium hydroxide was studied through a pozzolanic activity test. In addition, five different lime-pozzolan mixtures were prepared and studied for their compressive strength at four preset curing periods (one, three, six and twelve months). The results indicated that having the pozzolans similar chemical and mineralogical composition, the main parameter that affected their reactivity and the strength of the produced mixtures was the grain size distribution of the pozzolans within the range of 0-63μm.

1 Introduction

The properties of pozzolanic mortars and concretes have been studied extensively in the past, with the interest mainly concentrated on artificial pozzolanic additives. At the same time the role of natural pozzolans was undermined and therefore, no extended systematic studies on the role of natural pozzolans in lime mortars have been published. This is because only in the recent years traditional pozzolanic mortars started to be used in conservation, especially in renovation interventions [1-3]. As a consequence there is a considerable lack of standardization in the quality of pozzolans as raw materials, the preparation of the mixtures and the testing of the final products. This is the reason why almost all the reported results cannot be compared in a straightforward manner [1, 2].

Lately, in a growing number of papers the need for using materials similar to the original ones, avoiding modern binders and cements, is underlined [3-6]. This is mainly due to the high degree of compatibility to the archaeological and historical mortars in every aspect of materials performance. More specifically, besides the obvious chemical and mineralogical resemblance by using the same type of raw materials, lime-pozzolan mortars offer the advantage of mechanical compatibility, which contributes greatly to the life expansion of the interventions. Furthermore, the compatibility is very critical for the optimum performance of conservation mortars, considering the damages caused to cultural heritage monuments during the past decades, due to the extensive use of cement mixtures and their disadvantages in terms of incompatibility with porous stones, high salt content and very different elasticity [3, 7].

In this context the investigation of the currently available products of natural pozzolans and the properties they provide to lime mortars is significant for the conservation practise, which utilizes such materials [3,7]. The present study focuses on the physiochemical characterisation of five commercially available in the Greek market natural pozzolans and their effect on the mechanical properties of the setting products when they are used as additives in lime mortars.

2 Experimental methodology

2.1 Materials

Aiming to ensure the quality of lime, the lime putty (L) was prepared in the laboratory from chemical-grade $Ca(OH)_2$ powder and left for six months to mature, instead of using a ready made commercial product. The aggregate fraction (S) consisted of standard silicate sand (quartz) [8] and it was free from reactive components.

The pozzolans studied originated from three different geographic areas of Greece, which contain volcanic rock formations. Five pozzolans, available as market products, were collected: P1 (fine) and P2 (coarse) from Milos island, P3 (fine) and P4 (coarse) from North Greece mainland and P5 (coarse) from Kimolos island. The materials were sieved and the fraction between 0-63 μm was used in the experimental procedure (P1-f, P2-f, P3-f, P4-f and P5-f).

Chemical analysis of the raw materials was performed using the energy dispersive X-ray analyser attached to the scanning electron microscope (SEM/EDX). Moreover, the mineralogical composition of the raw materials and the setting products of the mortars produced were studied by X-ray diffraction (XRD). Finally, the loss on ignition (LOI) was determined based on the provisions of EN 196-2 standard [9].

The relevant ability of the different pozzolans to react with lime was determined through a pozzolanic activity test, in a saturated calcium hydroxide solution [10]. This test provides a comparative and indirect way to evaluate the consumption rate of lime due to the reaction with the pozzolanic material and the formation of the calcium aluminium and calcium silicate hydrates (C-A-H, C-S-H). The experimental procedure was performed at 40^{o}C, using a sample to solution ratio equal to 1/40 (w/v).

2.2 Mortar mixtures

Five different mortar mixtures were prepared, by mixing equal parts (w/w) of lime putty and pozzolans. The nomenclature for mixtures follows the one of the pozzolans, so M1 stands for the pozzolan P1-f, M2 for P2-f etc. The binder to aggregate ratio was set to 1:3, as this is indicated by relevant standards [8] and commonly appearing in historical and modern mortar applications [11]. The quantity of water used for the mixtures was determined through workability measurements [12] and was set to 0.5 water/binder ratio. The mixtures were placed in cylindrical moulds [13] and cured at 98 % RH conditions.

At preset time periods (28, 90, 180 and 365 days), five specimens from each mixture were used for determining their compressive strength [4, 13-15], using a displacement rate of 218 μm/min.

3 Results and discussion

3.1 Characterization of raw materials and reactivity test of pozzolans

Table 1 Chemical composition of raw materials expressed as wt % of their oxides

	Al_2O_3	Si_2O	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Cl	TiO_2	LOI
P1-f	12.36	71.03	2.18	1.49	0.71	2.25	2.88	nd	0.15	nd	6.95
P2-f	12.23	72.51	1.54	1.18	nd	2.51	2.95	nd	0.17	0.29	6.63
P2 bulk	12.46	71.98	1.24	1.47	nd	2.84	2.82	nd	0.16	0.27	6.76
P3-f	13.51	71.23	1.62	0.95	0.51	1.87	2.84	nd	0.18	nd	7.29
P4-f	14.41	69.21	1.38	0.95	nd	1.23	2.49	nd	0.13	1.50	8.71
P4 bulk	14.22	69.43	1.65	1.10	nd	1.21	2.47	1.22	0.16	nd	8.54
P5-f	14.84	67.78	1.84	2.16	1.51	2.18	2.14	nd	0.11	0.25	7.20
P5 bulk	14.96	69.16	2.24	1.35	2.03	1.51	2.01	nd	0.13	0.29	6.33
Sand	1.87	97.00	nd	nd	nd	nd	0.88	nd	nd	nd	0.26
Lime	0.63	1.08	nd	97.10	1.19	nd	nd	nd	nd	nd	nd

Chemical analysis showed that all pozzolans have similar composition (Table 1), typical for volcanic earth formations.

Based on the diffraction patterns (Fig. 1), the pozzolans present an amorphous character, containing small amounts of quartz and secondary mineral phases. The pozzolan from the North Greece (P3, P4) present some faint peaks attributed to chlorites, illite and kaolinite, while the pozzolan from Kimolos (P5) contains small amounts of montmorilonite. The above results are compatible with those of other researchers [16].

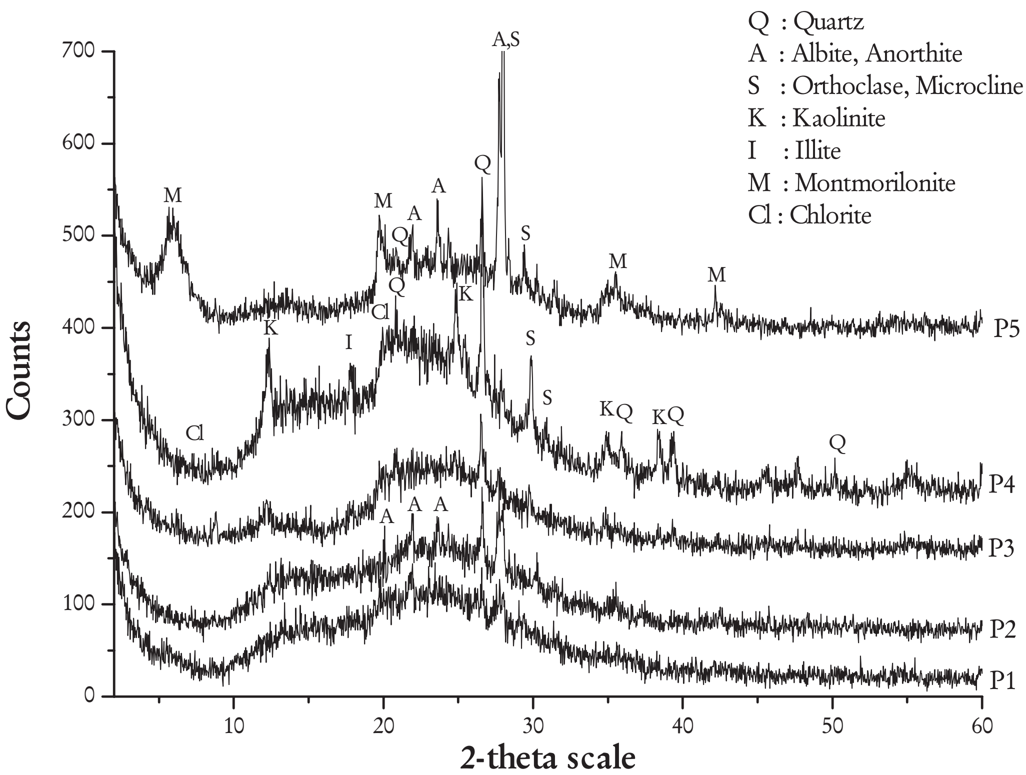

Fig. 1 Representative diffraction patterns of the fine fraction (0-63 μm) of the pozzolanic materials

The pozzolanic activity tests (Fig. 2) showed that all pozzolanic materials exhibited high reactivity, except that of P2 (from Milos), which exhibited the lowest reactivity. The one from Kimolos (P5-f) seemed to react faster during the first 24hours, but at the end it consumed relatively smaller amount of lime than the pozzolans from North Greece (P3-f and P4-f). Finally, it is noteworthy that the fragment P4-f, which was derived by sieving the initial bulk material, exhibits higher reactivity than P3-f that is originally provided in the fine fraction (0-63μm).

3.2 Setting products and compressive strength

From the diffraction patterns is derived that the majority of $Ca(OH)_2$ (portlandite) has been consumed between the third and sixth month, depending on the relevant reactivity of each pozzolan. Mixture M2 forms an exception, since it contains the less reactive pozzolan (P2-f). Although calcite is detected in all mixtures, the main setting products are formed through the hydration process, such as calcium aluminum oxide carbonate hydrate, calcium aluminum oxide hydrate and calcium silicon hydrate (Fig. 3) [17]. The mineralogical analysis on mortars after 12 months of curing is presented in Fig. 3.

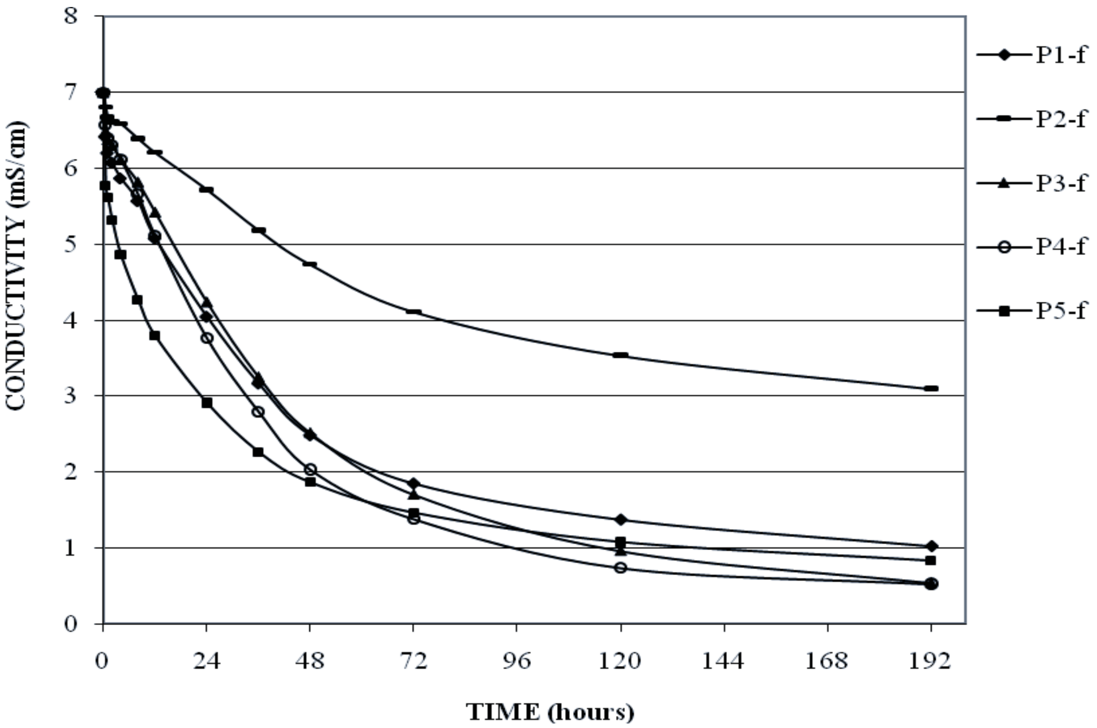

Fig. 2 Reactivity of the fine fractions of pozzolans used for the mortar syntheses

The formation of those setting products influences the mechanical properties of the mixtures, since they create a more dense and coherent microstructure. In Fig. 4, it is observed that the addition of different pozzolans greatly affects the strength of mortars during the first 28 days, while in three months the mixtures present very similar compression values. The mixtures M3 and M4 reached their maximum values in six months, by contrast to M1 and M5 that continuously increase their strength up to twelve months, presenting about 12 % higher values than M4. Mixture M2 presented the lowest strength values, corresponding to the lowest lime consumption during pozzolanic activity test. It is worth noting that neither the differentiation of the strength at the 28 days nor the final strength values correspond to the behaviour of pozzolans during pozzolanic activity test.

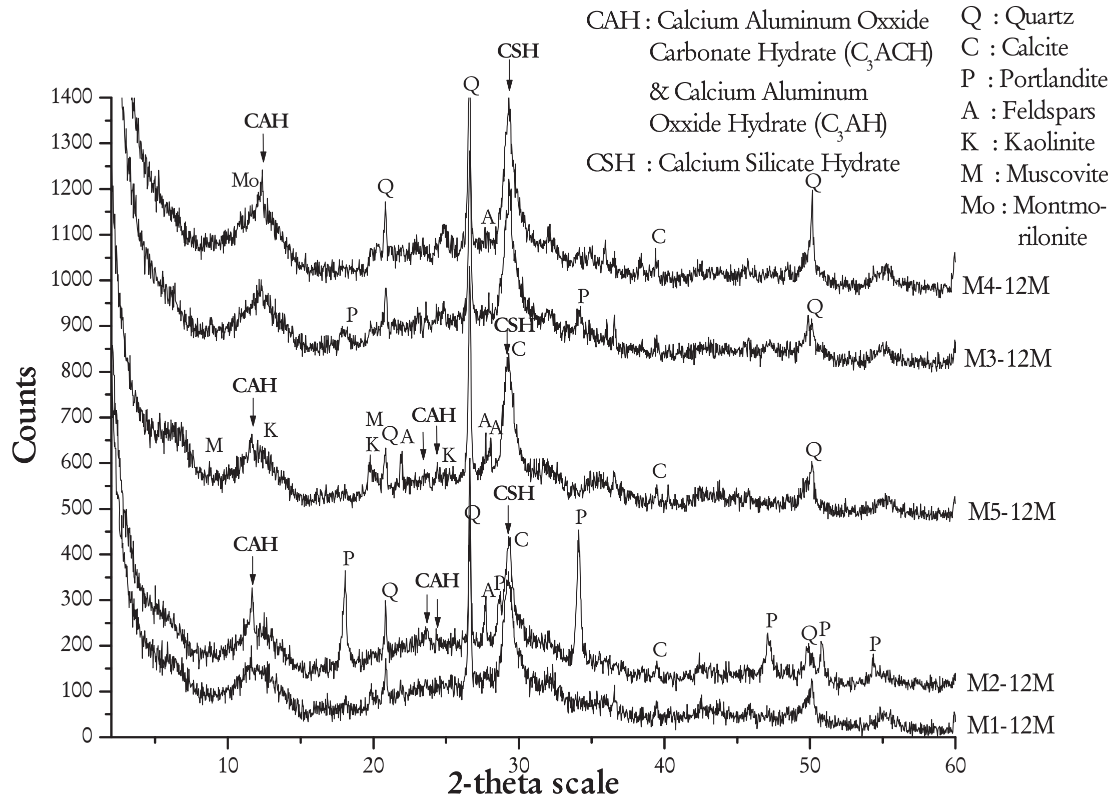

Fig. 3 Diffraction patterns of mortars cured for twelve months, presenting the main peaks of the setting products formed

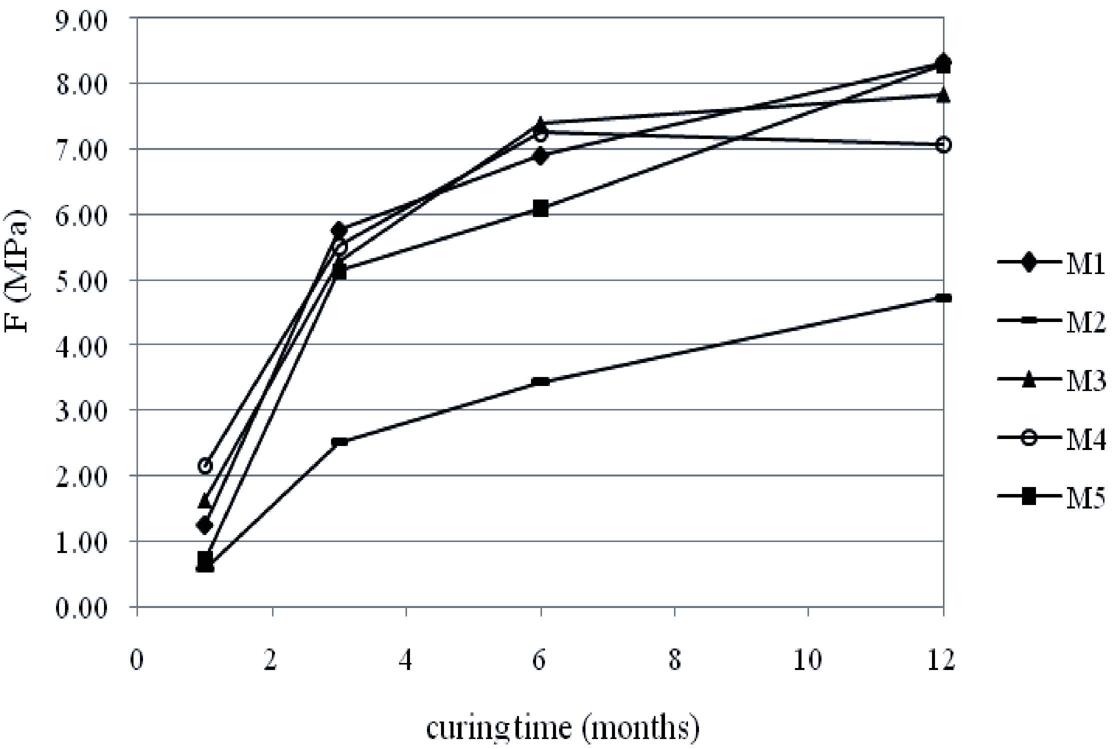

Fig. 4 Compressive strength of mortars

Considering that all pozzolans have similar mineralogy and present very similar behaviour during pozzolanic activity test it was assumed that the differences observed in mechanical properties should be attributed to the grain size distribution of different pozzolans within the range of 0-63 μm. Indeed, the examination of the pozzolans in SEM and the measurement of individual grains supported the above assumption, highlighting the differences between pozzolans P1-f and P2-f (Fig. 5). Although below 63μm, pozzolan P2-f presents a distribution with the majority of grains close to 63 μm. In contrast, pozzolan P1-f presents the majority of its grains below 20 μm.

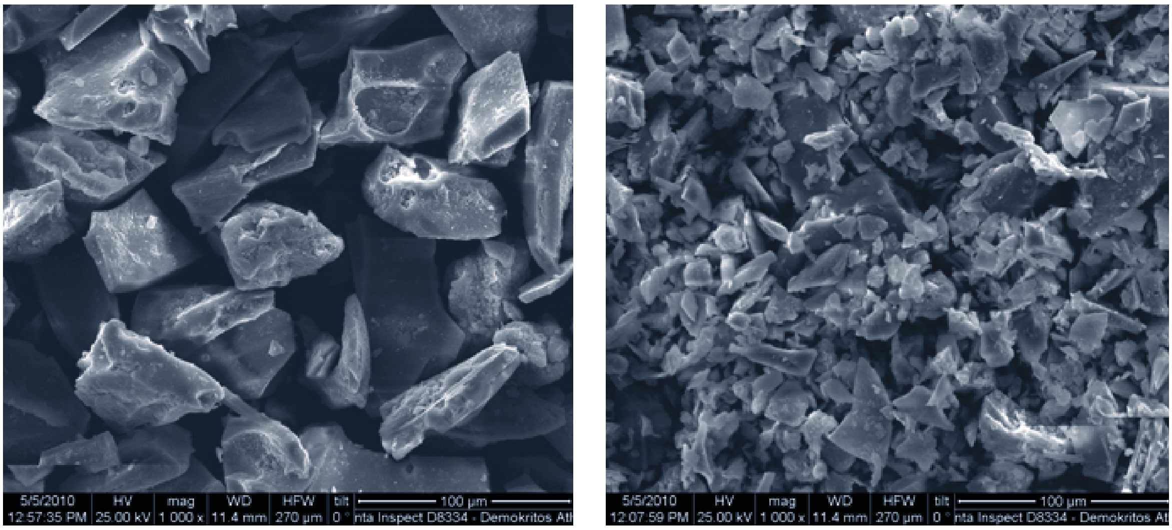

Fig. 5 SEM microphotographs of the pozzolans P1-f (right) and P2-f (left) exhibiting their different grain size (scale at 100μm)

Therefore, it seems that apart from the mineralogy of pozzolans, the development rate of strength is mainly affected by their grain size distribution within the range of 0-63 μm, giving preference to distributions of smaller grain size. In the above context, the use of the same amount of water in the mixtures studied could also affect their strength values, by slightly modifying the porosity of the mixtures.

4 Conclusions

From the interpretation of chemical and mineralogical composition of the pozolans it appears that they do not differ significantly. They are all amorphous materials of volcanic origin and contain some small amounts of clay phases. Similarly, based on the reduction of conductivity values during pozzolanicity test, it was proved that four out of the five materials presented almost similar reactivity behaviour.

In contrast, the examination of the pozzolans in SEM showed that, although all materials had grain size bellow 63 μm, they were presented different distributions within the range of 0-63μm. This parameter can explain the observed differences in the pozzolanicity test and compressive strength values of mortar mixtures. Therefore, it was proved that apart from the curing period of mixtures, the main factor that affects their strength is the particle size of the pozzolans and especially their grain size distribution within the range of 0-63μm.

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